

CURABLE LIQUID RESIN COMPOSITION

5 The present invention relates to a curable liquid resin composition. More particularly, the present invention relates to a curable liquid resin composition suitable as a coating material such as a secondary material or a ribbon matrix material for optical fibers, particularly as a secondary material.

10 In the fabrication of optical fibers, a resin coating is applied for protection and reinforcement immediately after spinning molten glass fibers. As the resin coating, a structure in which a flexible primary coating layer is provided on the surface of a glass fiber and a rigid secondary coating layer is provided on the outside of the primary coating layer has been known. Before subjecting optical fibers provided with a resin coating to practical application, for example four or eight optical fibers are
15 arranged side by side on a plane and secured using a bundling material, thereby forming a ribbon structure with a rectangular cross-section. A resin composition for forming the first coating layer is called a primary material, a resin composition for forming the second coating layer is called a secondary material, and a material for binding several optical fibers is called a ribbon matrix material.

20 One of the functions of the secondary material and the ribbon matrix material is to act as strong protective films which do not cause an external load to be applied to the primary material in the lower layer and quartz glass fibers. Therefore, these materials are designed so as to have a glass transition temperature of more than room temperature and a high modulus of rigidity. However, when the secondary
25 material or the ribbon matrix material is cured during the production process, a residual stress may occur in the cured film due to cooling, shrinkage, or the like, and an external load may be applied to the lower layer without being absorbed, whereby a load is applied to the primary material in the lower layer. One of the phenomena caused by the load is damage to the primary material producing voids therein and peeling of the
30 primary material from the quartz glass, which is considered to be one of the causes for transmission loss.

 As technologies for reducing the thickness of coating layers while maintaining optical transmission characteristics, a coated optical fiber having a specific stress-relaxation time (Japanese Patent Application Laid-open No. 8-5877) and an
35 optical fiber with improved durability by providing an optical fiber primary coating layer with excellent stress-relaxation characteristics (Japanese Patent Application Laid-open No. 2001-31731) have conventionally been known. However, since these methods do

not necessarily provide sufficiently shortened stress-relaxation time, the above technical problem still remains to be solved.

A radiation-curable liquid resin composition comprising a polyurethane (meth)acrylate oligomer which has one branch point per molecule, has (meth)acrylic groups at two of the three molecular ends extending from this branch point, and does not have a (meth) acrylic group at the remaining end is disclosed in Japanese Patent Application Laid-open No. 2000-351818. Since the Young's modulus of the cured product obtained from this composition at 25°C is 1 MPa or less, the composition cannot be used as a secondary material.

Accordingly, an object of the present invention is to provide a curable liquid resin composition which after curing can be used as a protective film, particularly as a secondary material, and which is capable of forming a cured layer producing only a slight residual stress therein and easily absorbing external loads.

The above object can be achieved in the present invention by a curable liquid resin composition comprising the following components (A), (B), and (C):

- (A) 0.5-50 wt% of a urethane (meth)acrylate oligomer obtained from a polyol (a) having a branched structure comprising at least one branch point and at least three molecular chains extending from that branch point, said molecular chains having a molecular weight of 200 g/mol or more, including a hydroxyl group at the terminal of at least two molecular chains extending from the branch point, a polyisocyanate (b), and a hydroxyl group-containing (meth)acrylate (c);
- (B) 5-90 wt% of a polymerizable organic compound; and
- (C) 0.1-10 wt% of a polymerization initiator,

wherein the cured product has a Young's modulus of 350 MPa or more at 23°C.

Since a cured product produced from the curable liquid resin composition of the present invention has a short stress-relaxation time of less than 4 minutes, the cured product does not impose a great load to a primary material. In addition, the cured product has a high Young's modulus. Therefore, the curable liquid resin composition of the present invention is useful as a secondary material and a ribbon matrix material for optical fibers, particularly as a secondary material.

In one embodiment of the invention, the urethane (meth)acrylate oligomer (A) is obtained by reacting (a) the polyol with the branched structure (branched polyol), (b) the polyisocyanate, and (c) the hydroxyl group-containing (meth)acrylate by adjusting the raw material molar ratio so that hydroxyl groups originating from the polyol (a) may remain in the resulting oligomer. Preferably, almost

all to all hydroxyl groups originating from the polyol (a) react.

As a method of reacting these compounds, a method of reacting (a) the branched polyol, (b) the polyisocyanate, and (c) the hydroxyl group-containing (meth)acrylate all together; a method of reacting (a) the branched polyol with (b) the polyisocyanate, and reacting the resulting product with (c) the hydroxyl group-containing (meth)acrylate; a method of reacting (b) the polyisocyanate with (c) the hydroxyl group-containing (meth)acrylate, and reacting the resulting product with (a) the branched polyol; a method of reacting (b) polyisocyanate with (c) the hydroxyl group-containing (meth)acrylate, reacting the resulting product with (c) the polyol, and further reacting the resulting product with (c) the hydroxyl group-containing (meth)acrylate; and the like can be given.

In the reaction of these compounds, it is preferable to use a urethanization catalyst such as copper naphthenate, cobalt naphthenate, zinc naphthenate, di-n-butyltin dilaurate, triethylamine, 1,4-diazabicyclo[2.2.2]octane, or 2,6,7-trimethyl-1,4-diazabicyclo[2.2.2]octane in an amount of 0.01-1 part by weight for 100 parts by weight of the total reactant. The reaction is carried out at a temperature of preferably 10-90°C, and particularly preferably 30-80°C.

In one embodiment of the invention, the branched polyol (a) is obtained by ring-opening polymerization of glycerol or sorbitol with at least one of ethylene oxide, propylene oxide, or butylene oxide.

In another embodiment of the invention, the branched polyol (a) is made in situ by reacting a polyol (a'), which comprises at least three hydroxyl groups and which is preferably a triol or a tetraol with a relatively low molecular weight, for example a triol such as Polyol TP30LW (ethoxylated trimethylolpropane) or a tetraol such as Polyol PP50 (ethoxylated pentaerythritol), both from Neste Oxo, with a polyisocyanate (b), at least one other polyol (a''), preferably a diol, and a hydroxyl group containing (meth)acrylate (c). In this embodiment, branched polyols (a) are formed by reaction of the polyol (a') with the polyisocyanate, and subsequently with the at least one other polyol (a''), preferably a diol, which forms the molecular chain extending from the branch point. Herein the at least one other polyol (a'') can for example be chosen from the group of polyols described below as "(a2)" ("polyols other than (a) or mixtures of polyols").

Subsequently the branched polyol (a) thus formed is reacted with (b) a polyisocyanate and (c) a hydroxyl group containing (meth)acrylate to form the urethane (meth)acrylate oligomer (A). The branched polyol (a) of this embodiment thus exists of a branch point (core), being formed by the polyol (a'), molecular chains extending from the branch

point, being formed by the at least one other polyol (a''), preferably a diol, and reactive end groups from the hydroxyl containing (meth)acrylate. The polyisocyanate connects the branch point (core), the molecular chain extending from the branch point and the (meth)acrylate reactive group.

5 Depending on the ratios between the polyol (a'), the at least one other polyol (a''), preferably diol, the polyisocyanate (b) and the hydroxyl containing (meth)acrylate (c), mixtures of difunctional and polyfunctional (meth)acrylates can be formed. Thus, after the formation of the branched polyol (a) which forms (A) after reaction with the hydroxyl containing (meth)acrylate, the reaction mixture may also still
10 contain free diols (a''), which may react with the hydroxyl containing (meth)acrylate to form a difunctional oligomer.

 As the polyol (a') used in the above embodiment low molecular polyols can be used which are usually liquid at room temperature and thus easy to handle during synthesis. Reactions with said polyols can usually be carried out without
15 a solvent. Also, said polyols relatively cheap and easily available polyols can be used. A large variety of branched oligomers, or mixtures of branched oligomers and linear oligomers can be made in one pot by varying the type of polyol (a') (e.g. number of hydroxyl groups, molecular weight), the type of the at least one other polyol (a''), preferably a diol (e.g. molecular weight), and the ratios between the reactants.
20 Therefore, depending on the requirements of the oligomer, many different systems can be made.

 The molecular weight of at least three molecular chains extending from the branch point of the branched polyol (a) is preferably 500 g/mol or more, more preferably 700 g/mol or more. In one embodiment of the invention the molecular weight
25 of at least three molecular chains extending from the branch point of the branched polyol (a) is preferably 1000 g/mol or more. The molecular weight of at least three molecular chains extending from the branch point of the branched polyol (a) is preferably 10,000 g/mol or less, more preferably 5,000 g/mol or less, most preferably 3000 g/mol or less. In one embodiment of the invention the molecular weight of at least
30 three molecular chains extending from the branch point of the branched polyol (a) is preferably 2,000 g/mol or less.

 Although there are no specific limitations, the number average molecular weight of the polyol (a) is preferably from 1,500 to 20,000 g/mol, more preferably from 1,500 to 12,000 g/mol, most preferably from 2,000 to 10,000 g/mol, and
35 particularly preferably from 2,500 to 8,000 g/mol.

 The number average molecular weight per one side chain of the

polyol (a) is preferably from 500 to 2,000 g/mol, and more preferably from 1,000 to 1,500 g/mol.

Preferably, the branched polyol (a) has 3-6 molecular chains extending from the branch point, more preferably 3 or 4 molecular chains extending from the branch point. At least two, preferably at least three, more preferably all molecular chains extending from the branch point include a terminal hydroxyl group.

As commercially available branched polyols, which can be reacted with the polyisocyanate (b) and the hydroxyl group containing (meth)acrylate (c), products manufactured by Daiichi Kogyo Seiyaku Co., Ltd., such as G3000; Asahi Glass Urethane Co., Ltd.; or Sanyo Chemical Industries, Ltd. such as Sannix GL-3000, Sannix GP-3000, Sannix GP-3700M, Sannix GP-4000, Sannix GEP-2800, Sannix GP-600 and Sannix GP-1000, Newpol TL-4500N, and the like can be given. In another embodiment of the invention, wherein apart from a polyol (a') at least one other polyol (a''), preferably a diol, is used to form the branched polyol (a), relatively small branched polyols, such as Polyol TP30LW (ethoxylated trimethylolpropane) or a tetraol such as Polyol PP50 (ethoxylated pentaerythritol), both from Neste Oxo, Sannix TP-400, Sannix GP-250, Sannix GP-400, may be used as the polyol (a') with a relatively low molecular weight.

Polyols other than (a) or mixtures of polyols may be added to (a). These other polyols or mixtures of polyols are defined as (a2). Examples of (a2) include aliphatic or cyclic polyether diols, polyester diols, polycarbonate diols, and polycaprolactone diols. There are no specific limitations to the manner of polymerization of the structural units of these polyols. These polyols may be any of a random polymer, block polymer, or a graft polymer. As examples of aliphatic polyether diols, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, polyether polyols obtained by the ring-opening copolymerization of two or more ion-polymerizable cyclic compounds, and the like can be given. As examples of the ion-polymerizable cyclic compounds, cyclic ethers such as ethylene oxide, propylene oxide, 1,2-butylene oxide, butene-1-oxide, isobutene oxide, 3,3-bis(chloromethyloxy)tetrahydrofuran, tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, dioxane, trioxane, tetraoxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl methacrylate, allyl glycidyl ether, allyl glycidyl carbonate, butadiene monoxide, isoprene monoxide, vinyl oxetane, vinyl tetrahydrofuran, vinyl cyclohexene oxide, phenyl glycidyl ether, butyl glycidyl ether, and glycidyl benzoate can be given. Moreover, polyether polyols obtained by ring-opening

copolymerization of the above ion-polymerizable cyclic compounds with monomers, for example, cyclic imines such as ethyleneimine, cyclic lactone acids such as β -propylactone and glycolic acid lactide, and dimethylcyclopolsiloxanes can be used.

As examples of specific combinations of two or more ion-polymerizable cyclic

5 compounds, combinations of tetrahydrofuran and propylene oxide, tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydrofuran and 3-methyltetrahydrofuran, tetrahydrofuran and ethylene oxide, propylene oxide and ethylene oxide, butene-1-oxide and ethylene oxide, a ternary copolymer of tetrahydrofuran, butene-1-oxide, and ethylene oxide, and the like can be given. The ring-opening copolymer of these ion-polymerizable cyclic
10 compounds may be either a random copolymer or a block copolymer.

These polyether polyols are commercially available as PTMG650, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), PEG1000, Unisafe DC1100, DC1800 (manufactured by Nippon Oil and Fats Co., Ltd.), PPTG2000, PPTG1000, PTG400, PTGL2000 (manufactured by Hodogaya Chemical
15 Co., Ltd.), Z-3001-4, Z-3001-5, PBG2000A, PBG2000B (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), Acclaim polypropylene glycols, such as Acclaim 4200 and Acclaim 200, Desmophen 2061BD (all manufactured by Bayer), and the like.

As examples of cyclic polyether polyols, alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of bisphenol F, hydrogenated bisphenol A,
20 hydrogenated bisphenol F, alkylene oxide addition diol of hydrogenated bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol F, alkylene oxide addition diol of hydroquinone, alkylene oxide addition diol of naphthohydroquinone, alkylene oxide addition diol of anthrahydroquinone, 1,4-cyclohexanediol and alkylene oxide addition diol thereof, tricyclodecanediol, tricyclodecanedimethanol, pentacyclopentadecanediol,
25 pentacyclopentadecanedimethanol, and the like can be given. Of these, alkylene oxide addition diol of bisphenol A, alkylene oxide addition diol of hydrogenated bisphenol A, and tricyclodecanedimethanol are preferable. These polyols are commercially available as Uniol DA400, DA700, DA1000, DB400 (manufactured by Nippon Oil and Fats Co., Ltd.), N1162 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.),
30 tricyclodecanedimethanol (manufactured by Mitsubishi Chemical Corp.), and the like.

As examples of the polyester polyol, polyester polyols obtained by reacting a polyol with a diacidic base and the like can be given. Examples of the above polyol include ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, neopentyl
35 glycol, 1,4-cyclohexanedimethanol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, and 2-methyl-1,8-octanediol. As examples of dibasic acids, phthalic acid, isophthalic acid,

terephthalic acid, maleic acid, fumaric acid, adipic acid, and sebacic acid can be given. These polyester diols are commercially available as Kurapol P-2010, PMIPA, PKA-A, PKA-A2, PNA-2000 (manufactured by Kuraray Co., Ltd.), and the like.

As examples of polycarbonate polyols, polycarbonate of
5 polytetrahydrofuran, polycarbonate of 1,6-hexanediol, and the like can be given. As commercially available products of polycarbonate polyols, DN-980, 981, 982, 983 (manufactured by Nippon Polyurethane Industry Co., Ltd.), PC-8000 (manufactured by PPG), PC-THF-CD (manufactured by BASF), and the like can be given.

As examples of polycaprolactone diols, polycaprolactone diols
10 obtained by reacting ϵ -caprolactone and diols such as ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,2-polybutylene glycol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, and 1,4-butanediol can be given. These diols are commercially available as PLACCEL 205, 205AL, 212, 212AL, 220, 220AL
15 (manufactured by Daicel Chemical Industries, Ltd.), and the like.

A number of polyols (a2) other than those illustrated above may be used. As examples of such other polyols, ethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, dimethylol compound of dicyclopentadiene, tricyclodecanedimethanol, β -methyl- δ -valerolactone,
20 hydroxy-terminated polybutadiene, hydroxy-terminated hydrogenated polybutadiene, castor oil-modified polyol, diol-terminated compound of polydimethylsiloxane, polydimethylsiloxanecarbitol-modified diol, and the like can be given.

In addition to the combined use of polyols, diamines can be used in combination with polyols. As examples of diamines, ethylenediamine,
25 tetramethylenediamine, hexamethylenediamine, p-phenylenediamine, 4,4'-diaminodiphenylmethane, diamines containing a hetero atom, polyether diamines, and the like can be given.

Of the above polyols (a2), polyether diols, alkylene oxide addition diol of bisphenol A, and alkylene oxide addition diol of hydrogenated bisphenol A are
30 preferable. These diols are commercially available as PTMG650, PTMG1000, PTMG2000 (manufactured by Mitsubishi Chemical Corp.), Uniol DA400, DA700, DA1000, DB400 (manufactured by Nippon Oil and Fats Co., Ltd.), and N1162 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.).

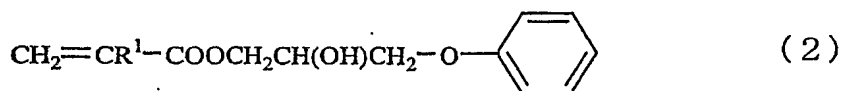
The number average molecular weight of the other polyol component
35 (a2) is 300-5,000, preferably 300-2,000, and more preferably 300-1,000.

As the polyisocyanate of the component (b), diisocyanates are

preferable. As examples of the diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 1,3-xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-
 5 dimethylphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, methylenebis(4-cyclohexylisocyanate), 2,2,4-trimethylhexamethylene diisocyanate, bis(2-isocyanate ethyl)fumarate, 6-isopropyl-1,3-phenyl diisocyanate, 4-diphenylpropane diisocyanate, lysine diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated xylylene diisocyanate,
 10 tetramethylxylylene diisocyanate, 2,5(or 6)-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, and the like can be given. Of these, 2,4-tolylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and methylenebis(4-cyclohexylisocyanate) are particularly preferable.

These polyisocyanates (b) may be used either individually or in
 15 combinations of two or more.

As examples of the hydroxyl group-containing (meth)acrylate (c), 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 2-hydroxy-3-phenyloxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, 2-hydroxyalkyl(meth)acryloyl phosphate, 4-hydroxycyclohexyl
 20 (meth)acrylate, 1,6-hexanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, and (meth)acrylates shown by the following formulas (1) and (2) can be given:



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wherein R^1 represents a hydrogen atom or a methyl group and n is an integer from 1 to
 15.

Compounds obtained by the addition reaction of (meth)acrylic acid and a compound containing a glycidyl group such as alkyl glycidyl ether, allyl glycidyl
 30 ether, or glycidyl (meth)acrylate can also be used as the hydroxyl group-containing (meth)acrylate. Of these (meth)acrylates containing a hydroxyl group, 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate are particularly preferable.

These hydroxyl group-containing (meth)acrylates (c) may be used either individually or in combinations of two or more.

In one embodiment of the invention the molar ratio of the raw materials is adjusted during preparation of the urethane (meth)acrylate oligomer (A) so
5 that almost all to preferably all hydroxyl groups originating from the polyol (a) are reacted with the diisocyanate (b) and the hydroxyl group containing (meth)acrylate (c). In said embodiment only small amounts of hydroxyl groups may remain.

In another embodiment of the invention it is preferable to adjust the raw material molar ratio so that part of the hydroxyl groups originating from the polyol
10 (a) does not react with the diisocyanate (b) and the hydroxyl group containing (meth)acrylate (c) but is still present as a hydroxyl group in the oligomer (A).

The urethane (meth)acrylate of component (A) is added to the curable liquid resin composition of the present invention in an amount of 0.5-50 wt%, preferably 3-45 wt%, and more preferably 5-40 wt%. If the content is less than 0.5
15 wt%, coatability may be impaired. If the content exceeds 50 wt%, the Young's modulus of elasticity of the cured products decreases. In one embodiment of the invention the urethane (meth)acrylate oligomer (A) is added as the main component of the total amount of urethane (meth)acrylate oligomer in the curable liquid resin composition.

In another embodiment of the invention the urethane (meth)acrylate
20 oligomer (A) is added as a modifier, for example a rheology modifier, of the main component of the urethane (meth)acrylate oligomer. This embodiment is aimed at providing a curable liquid resin composition, in particular a secondary resin composition, with improved processability. The preparation of coated optical fibers today involves passing the fibers through a coating die mounted within a device known
25 as a draw tower, followed by curing the applied resin compositions. In wet-on-wet applications secondary resin compositions are applied to an optical glass fiber simultaneously with a primary resin composition, after which both resin compositions are simultaneously cured. Typically, the rheological properties of primary resin compositions and secondary resin compositions are different, i.e. said compositions
30 feature a limited rheological compatibility. This may cause certain problems. The drag flow induced by the moving fiber at high drawing speeds gives rise to high shear rates, typically being between 10^5 and 10^6 s⁻¹ at the location near the exit of the coating cup. Optical fiber resin compositions usually show complicated non-Newtonian behavior as shear rate increases. Due to this, processability instabilities often occur during fiber
35 production, in particular in wet-on-wet applications where primary resin compositions and secondary resin compositions with different rheological properties are applied.

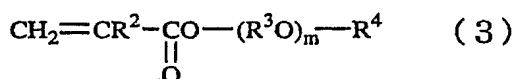
Another significant problem concerns the degree of uniformity in the coating after curing. More specifically, in high quality coated fibers, the thickness of the coating layer possesses a high degree of uniformity along the length of the fiber. At high speeds, however, typically above about 25 m/sec, a combination of high fiber speed, relatively
5 small clearance between the outer surface of the fiber and die, die length, pressure exerted on the composition as it is fed into the die, and properties of the uncured coating compositions, can result in unacceptably low levels of uniformity in a cured coating. Optical fibers with low levels of coating uniformity can present problems when one desires to splice two optical fibers together. Non-uniformity may also translate into
10 data transmissions problems after installation into a data network, e.g., signal attenuation. One means of addressing processing instability is to control, in some manner, the rheological properties of the curable liquid secondary resin composition.

In the above embodiment, wherein the urethane (meth)acrylate oligomer (A) is added as a modifier, for example a rheology modifier, the main
15 component of the urethane (meth)acrylate oligomer is preferably a urethane (meth)acrylate oligomer based on a diol, to which the urethane (meth)acrylate oligomer (A) is added in an amount of for example 0.5-10 wt% in order to obtain more favourable rheological properties if the liquid resin. In the embodiment of the invention, wherein the urethane (meth)acrylate oligomer (A) is added as a rheology modifier, the steady
20 state compliance J_e , which is a measure of the elasticity of the resin, is preferably 2 MPa^{-1} or more, more preferably 3 MPa^{-1} or more, most preferably 4 MPa^{-1} or more, particularly preferably 5 MPa^{-1} or more.

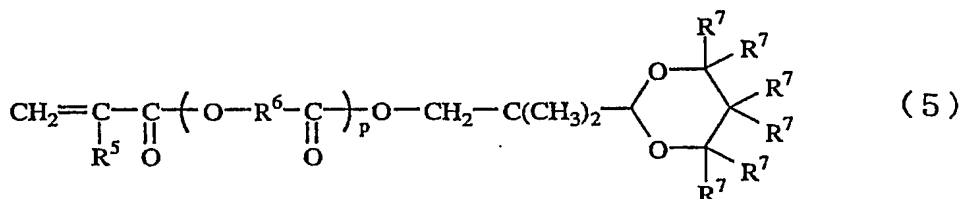
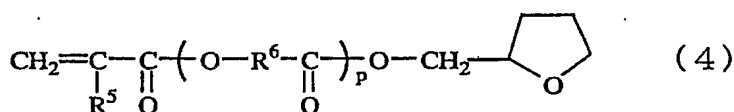
A urethane (meth)acrylate obtained by reacting 1 mol of diisocyanate with 2 mols of (meth)acrylate containing a hydroxyl group may be added to the curable
25 liquid resin composition of the present invention. Given as examples of such a urethane (meth)acrylate are the reaction product of hydroxyethyl (meth)acrylate and 2,4-tolylene diisocyanate, reaction product of hydroxyethyl (meth)acrylate and 2,5 (or 6)-bis(isocyanatemethyl)-bicyclo[2.2.1]heptane, reaction product of hydroxyethyl (meth)acrylate and isophorone diisocyanate, reaction product of hydroxypropyl
30 (meth)acrylate and 2,4-tolylene diisocyanate, and reaction product of hydroxypropyl (meth)acrylate and isophorone diisocyanate.

A polymerizable monofunctional compound is blended with the liquid curable resin composition of the present invention as component (B). As examples of the monofunctional compound, N-vinylpyrrolidone, lactams containing a vinyl group
35 such as N-vinylcaprolactam, (meth)acrylates containing an alicyclic structure such as isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, and

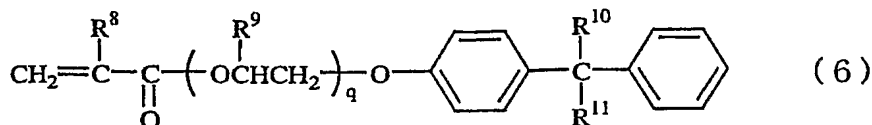
dicyclopentanyl (meth)acrylate, benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloylmorpholine, vinyl imidazole, vinyl pyridine, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, 5 butyl (meth)acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, undecyl (meth)acrylate, dodecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl(meth)acrylate, phenoxyethyl(meth)acrylate, polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, diacetone(meth)acrylamide, isobutoxymethyl(meth)acrylamide, 15 N,N-dimethyl(meth)acrylamide, t-octyl(meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, 7-amino-3,7-dimethyloctyl (meth)acrylate, N,N-diethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl 20 vinyl ether, 2-ethylhexyl vinyl ether, and compounds shown by the following formulas (3) to (6) can be given;



wherein R² represents a hydrogen atom or a methyl group, R³ represents an alkylene group having 2-6, and preferably 2-4 carbon atoms, R⁴ represents a hydrogen atom or 25 an alkyl group having 1-12, and preferably 1-9 carbon atoms, and m is an integer from 0 to 12, and preferably from 1 to 8.



wherein R⁵ represents a hydrogen atom or a methyl group, R⁶ represents an alkylene group having 2-8, and preferably 2-5 carbon atoms, R⁷ represents a hydrogen atom or a methyl group, and p is preferably an integer from 1 to 4.



- 5 wherein R⁸, R⁹, R¹⁰, and R¹¹ individually represent a hydrogen atom or a methyl group, and q is an integer from 1 to 5.

Of these monofunctional compounds (B), N-vinylpyrrolidone, lactams containing a vinyl group such as N-vinylcaprolactam, isobornyl (meth)acrylate, lauryl acrylate, and a compound of the above formula (6) are preferable.

- 10 These monofunctional compounds (B) are commercially available as IBXA (manufactured by Osaka Organic Chemical Industry Co., Ltd.), Aronix M-111, M-113, M-114, M-117, TO-1210, Aronix M-110 (manufactured by Toagosei Co., Ltd.), and the like.

- 15 In view of reduction in the stress relaxation time, the amount of the polymerizable monofunctional compound (B) in the curable liquid resin composition of the present invention is preferably 5-90 wt%, and more preferably 10-80 wt%.

The curable liquid resin composition of the present invention comprises a polymerization initiator as component (C). As the polymerization initiator, a heat polymerization initiator or a photoinitiator can be used.

- 20 In the case of curing the curable liquid resin composition of the present invention using heat, a heat polymerization initiator such as a peroxide or azo compound is used. As specific examples of the heat polymerization initiator, benzoyl peroxide, t-butyloxybenzoate, and azobisisobutyronitrile can be given.

- 25 In the case of curing the curable liquid resin composition of the present invention using light, a photoinitiator is used. In addition, a photosensitizer is preferably added as required. As examples of photoinitiators, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenylacetophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3-methylacetophenone, 4-chlorobenzophenone, 4,4'-dimethoxybenzophenone, 4,4'-diaminobenzophenone, Michler's ketone, benzoin propyl ether, benzoin ethyl ether, 30 benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, thioxanethone, diethylthioxanethone, 2-isopropylthioxanethone, 2-chlorothioxanethone, 2-methyl-1-[4-(methylthio)phenyl]-2-

morpholino-propan-1-one, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide; IRGACURE 184, 369, 651, 500, 907, CGI 1700, CGI 1750, CGI 1850, CG24-61 (manufactured by Ciba Specialty Chemicals Co.); Lucirin LR8728 (manufactured by BASF); Darocure 1116, 1173
5 (manufactured by Merck), Ubecryl P36 (manufactured by UCB), and the like can be given. As examples of photosensitizers, triethylamine, diethylamine, N-methyldiethanolamine, ethanolamine, 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate; Ubecryl P102, 103, 104, 105 (manufactured by UCB); and the
10 like can be given.

In the case of curing the curable liquid resin composition of the present invention using both heat and ultraviolet rays, the heat polymerization initiator and the photoinitiator may be used in combination. The polymerization initiator (C) is used in the curable liquid resin composition of the present invention in an amount of
15 preferably 0.1-10 wt%, and particularly preferably 0.5-7 wt%.

A polymerizable polyfunctional compound may further be incorporated in the curable liquid resin composition of the present invention as component (D). As examples of the polyfunctional compound (D), trimethylolpropane tri(meth)acrylate, trimethylolpropanetrioxymethyl (meth)acrylate, pentaerythritol
20 tri(meth)acrylate, ethylene glycol di(meth)acrylate, triethylene glycol diacrylate, tetraethylene glycol di(meth)acrylate, tricyclodecanedioldimethanol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, both terminal (meth)acrylic acid
25 addition compound of bisphenol A diglycidyl ether, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, polyester di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tricyclodecanedioldimethanol di(meth)acrylate, di(meth)acrylate of ethylene oxide or propylene oxide addition diol of bisphenol A, di(meth)acrylate of
30 ethylene oxide or propylene oxide addition diol of hydrogenated bisphenol A, epoxy(meth)acrylate prepared by the addition of (meth)acrylate to diglycidyl ether of bisphenol A, triethylene glycol divinyl ether, and the like can be given.

Of these polymerizable polyfunctional compounds (D), tricyclodecanedioldimethanol di(meth)acrylate, di(meth)acrylate of ethylene oxide
35 addition diol of bisphenol A, and tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate are preferable.

As commercially available products of these polymerizable polyfunctional compounds (D), Yupimer UV, SA-1002 (manufactured by Mitsubishi Chemical Corp.), Aronix M-215, M-315, M-325, TO-1210 (manufactured by Toagosei Co., Ltd.), GX-8345 (manufactured by a Daiichi Kogyo Seiyaku Co., Ltd.), and the like
5 can be given.

These polymerizable polyfunctional compounds (D) are added to the curable liquid resin composition of the present invention in an amount of preferably 5-90 wt%, and particularly preferably 10-80 wt%. If the amount is less than 5 wt% or exceeds 90 wt%, application may become uneven due to changes in the application
10 form.

Various additives such as antioxidants, coloring agents, UV absorbers, light stabilizers, silane coupling agents, heat polymerization inhibitors, leveling agents, surfactants, preservatives, plasticizers, lubricants, solvents, fillers, aging preventives, wettability improvers, and coating surface improvers may be
15 optionally added to the curable liquid resin composition of the present invention, insofar as the characteristics of the composition are not adversely affected.

The curable liquid resin composition of the present invention is cured by heat or radiation. Radiation used herein refers to infrared rays, visible rays, ultraviolet rays, X-rays, electron beams, α -rays, β -rays, γ -rays, and the like.

The cured product of the curable liquid resin composition prepared according to the above-described method has a stress relaxation time of less than 4 minutes, preferably 3 minutes or less, and more preferably 2 minutes or less. If the stress relaxation time is 4 minutes or more, a coating stress may remain during manufacturing of fibers or during handling, resulting in problems, particularly, such as
20 formation of voids in the primary layer and peeling of the primary layer from quartz glass.

The cured products have a Young's modulus of elasticity of 350 MPa or more, preferably 400 MPa or more, more preferably 500 MPa or more at 23°C.

30 Examples

The present invention is described below in more detail by examples. However, the present invention is not limited to these examples. In the examples, "part(s)" refers to "part(s) by weight".

35 Synthesis (A-1)

A reaction vessel equipped with a stirrer was charged with 6.651 g of

isophorone diisocyanate, 0.024 g of 2,6-di-t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After the dropwise addition of 6.651 g of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 89.763 g of polypropylenetriol with a number average molecular weight of 6,000 (G3000 manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), the mixture was stirred at 70-75°C for three hours. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less. This liquid resin is called "oligomer (A-1)".

Synthesis (A-2)

A reaction vessel equipped with a stirrer was charged with 16.489 g of isophorone diisocyanate, 0.024 g of 2,6-di-t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After the dropwise addition of 8.666 g of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 74.633 g of a ring opening diol of tetrahydroxyfuran with a number average molecular weight of 2,000 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), the mixture was stirred at 70-75°C for three hours. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less. This liquid resin is called "oligomer (A-2)".

Synthesis (U-1)

A reaction vessel equipped with a stirrer was charged with 44.726 g of isophorone diisocyanate, 0.024 g of 2,6-di-t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After the dropwise addition of 35.063 g of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 20.099 g of ethylene oxide addition diol of bisphenol A with a number average molecular weight of 400 (manufactured by NOF Corporation), the mixture was stirred at 70-75°C for three hours. The reaction was terminated when the residual isocyanate content was 0.1 wt% or less. This liquid resin is called "oligomer (U-1)".

Synthesis (B-1)

A reaction vessel equipped with a stirrer was charged with 5.287 g of

2,4-tolylene diisocyanate, 0.024 g of 2,6-di- t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After the dropwise addition of 3.525 g of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 91.076 g of polypropylenetriol with a number average molecular weight of 6,000 (G3000 manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), the mixture was stirred at 70-75°C for three hours. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less. The liquid resin obtained in this manner is called "oligomer (B-1)".

Synthesis (B-2)

A reaction vessel equipped with a stirrer was charged with 13.480 g of 2,4-tolylene diisocyanate, 0.024 g of 2,6-di-t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After the dropwise addition of 8.990 g of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 77.420 g of a ring opening polymer of tetrahydroxyfuran with a number average molecular weight of 2,000 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), the mixture was stirred at 70-75°C for three hours. The reaction was terminated when the residual isocyanate concentration was 0.1 wt% or less. The liquid resin obtained in this manner is called "oligomer (B-2)".

Synthesis (U-2)

A reaction vessel equipped with a stirrer was charged with 42.806 g of 2,4-tolylene diisocyanate, 0.024 g of 2,6-di- t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After adding 57.082 g of hydroxyethyl acrylate dropwise while controlling the temperature at 20°C or less, the mixture was stirred for 3 hours at 70-75°C. The reaction was terminated when the residual isocyanate content was 0.1 wt% or less. The liquid resin obtained in this manner is called "urethane acrylate (U-2)".

Synthesis (U-3)

A reaction vessel equipped with a stirrer was charged with 42.15 g of 2,4-tolylene diisocyanate, 0.024 g of 2,6-di-t-butyl-p-cresol, 0.080 g of dibutyltin dilaurate, and 0.008 g of phenothiazine. The mixture was cooled with ice to 10°C or below while stirring. After adding 43.48 g of hydroxyethyl acrylate and 14.26 g of

hydroxyethyl propyl acrylate dropwise while controlling the temperature at 20°C or less, the mixture was stirred for three hours at 70-75°C. The reaction was terminated when the residual isocyanate content was 0.1 wt% or less. The liquid resin obtained in this manner is called "urethane acrylate (U-3)".

5

Test Example

Preparation of test film: The curable liquid resin composition was applied to a glass plate using an applicator bar for a thickness of 250 µm. The curable liquid resin composition was cured by irradiation of ultraviolet rays at a dose of 1 J/cm² in air to obtain a test film.

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1. Measurement of Young's modulus of elasticity: The test film was cut into a sample in the shape of a strip with a width of 6 mm and a length of 25 mm. The sample was subjected to a tensile test at a temperature of 23°C and a humidity of 50%. The Young's modulus was calculated from the tensile strength at a strain of 2.5% and a tensile rate of 1 mm/min.

15

2. Measurement of stress relaxation time: The above test film was cut into a sample in the shape of a strip with a width of 6 mm and a length of 25 mm. A strain of 5% was applied to the sample at a rate of 1,000 mm/minute at a temperature of 23°C and a humidity of 50%. Changes in the stress were monitored by suspending the cross head of a tensile tester (Autograph AGS-50G manufactured by Shimadzu Corp.). A period of time in which the stress was reduced to 37% of the initial stress was determined as the stress relaxation time.

20

3. Observation of void occurrence in primary material:

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3-1 Preparation of primary coating material

A reaction vessel equipped with a stirrer was charged with 6.6 parts of 2,4-tolylene diisocyanate, 0.015 part of 2,6-di-t-butyl-p-cresol, 0.48 part of dibutyltin dilaurate, 0.005 part of phenothiazine, and 16.2 parts of IBXA (manufactured by the Osaka Organic Chemical Industry, Ltd.). The mixture was cooled with ice to 10°C or less while stirring. After the dropwise addition of 2.9 parts of hydroxyethyl acrylate, while controlling the temperature at 20°C or less, the mixture was allowed to react for one hour while stirring. After the addition of 50.0 parts of polytetramethylene glycol with a number average molecular weight of 2,000 (manufactured by Mitsubishi Chemical Corp.), the mixture was stirred at 50-60°C for four hours. The reaction was terminated when the residual isocyanate content was 0.1 wt% or less. After the addition of 10.8

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parts of isobornyl acrylate (manufactured by Rohm and Haas Japan K.K.), 4.8 parts of vinylcaprolactam, 5.6 parts of lauryl acrylate, and 0.2 part of Irganox 1035 (manufactured by Ciba-Geigy Ltd.), the mixture was stirred at 40-50°C for 30 minutes. After the addition of 0.1 part of diethylamine while controlling the temperature at 30-40°C, the mixture was stirred for 30 minutes. Then, one part of bis-(2,6-methoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide and one part of Darocure 1173 (manufactured by Merck) were added while controlling the temperature at 50-60°C, and the mixture was stirred until a homogeneous transparent liquid was obtained. The primary coating material was thus obtained.

3-2 Fiber drawing

The primary coating material was applied to a glass fiber and cured using an optical fiber drawing equipment (manufactured by Yoshida Kogyo Co., Ltd.). The compositions of the Examples and Comparative Examples were applied to the cured primary material.

The optical fiber drawing conditions were as follows. The diameter of the glass fiber was 125 µm. The primary coating material was applied to the metal line and cured so that the diameter of the optical fiber was 200 µm after curing. The composition of the Example or Comparative Example was applied to the primary material thus formed so that the diameter was 250 µm after curing. As UV irradiation equipment, a UV lamp "SMX 3.5 kw" manufactured by ORC Corp. was used. Applicability was evaluated at an optical fiber drawing rate of 1,000 m/min.

3-3 Observation of void occurrence

After immersing the above fiber in hot water at a temperature of 60°C for 72 hours, void occurrence in the primary material was observed using a microscope and peeling of the primary material from the quartz glass was observed by the naked eye.

Judgement:

Samples with Young's modulus of elasticity of 350 Mpa or more, a stress relaxation rate of less than 4 minutes, and not possessing voids were judged as acceptable products.

Table 1.

	Example			Comparative Example				
	1	2	3	1	2	3	4	5
Oligomer/ urethane acrylate								
A-1	32.00		37.50	74.00				
A-2					32.00			
U-1	42.00				42.00			
B-1		48.40				62.90		
B-2							50.40	37.50
U-2		14.50					12.50	
U-3			34.70					34.70
Monomer								
Isobornyl acrylate	9.45	17.42	26.92	9.45	9.45	17.42	17.42	26.92
N-Vinylcaprolactam		8.71				8.71	8.71	
SA1002 ^{*1}	1.93	7.74		1.93	1.93	7.74	7.74	
Viscoat #700 ^{*2}	19.30			19.30	19.30			
Irgacure 184 ^{*3}	2.99	2.91	2.99	2.99	2.99	2.91	2.91	2.99
Sumilizer GA-80 ^{*4}	0.29	0.30	0.29	0.29	0.29	0.30	0.30	0.29

^{*1} Mitsubishi Chemical Co., Ltd.

^{*2} Osaka Organic Chemical Industry Ltd.

^{*3} Ciba Specialty Chemicals Co. Ltd.

5 ^{*4} Sumitomo Chemical Co., Ltd.

Table 2.

	Example			Comparative Example				
	1	2	3	1	2	3	4	5
Young's modulus of elasticity (MPa)	510	570	600	300	700	330	700	850
Stress relaxation rate (min)	1.8	1.4	1.8	1.1	4.2	0.8	4.5	5.3
Fiber void	Absent	Absent	Absent	Absent	Present	Absent	Present	Present
Judgement	Passed	Passed	Passed	Failed	Failed	Failed	Failed	Failed

As is clear from Tables 1 and 2, the resin compositions of the Examples exhibited a high stress relaxation rate and satisfactory Young's modulus of elasticity as a secondary material, showing that the compositions are free from defects such as void formation in the primary material and peeling of the primary material from quartz glass.

5 Synthesis of mixtures of di-, tri- and or tetrafunctional urethane acrylate oligomers from a triol and a diol or a tetraol and a diol

10 Irganox 1035 (0.09 wt%), isophorene diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL, 0.05 wt%) were put in a reactor with dry airflow, stirring and cooling to 10 °C. Subsequently the triol Polyol TP30 LW (an ethoxylated trimethylolpropane with OH number 629 from Neste Oxo) or the tetraol Polyol PP50 (an
15 ethoxylated pentaerythritol with OH number 638 from Neste Oxo) was added and the reactor was left stirring for 1 hour at 10 °C. 2-Hydroxyethyl acrylate (HEA) was then added through a dropping funnel at 10 °C. After approximately 1 hour the midpoint was reached, after which the reactor was heated to 20 °C. Subsequently the diol
20 Desmophen 2061BD (polypropylene glycol with $M_w = 2000$ g/mol, OH number 56.6, Bayer) was added, after which the reaction mixture was heated to 80 °C. The reaction was allowed to proceed until the NCO content was below 0.05 %. The polyols and diols, IPDI and HEA were added in stoichiometric amounts.

In Table 3 the oligomers prepared using the above method are listed. In Table 4 the molecular weight of the oligomers is given, as well as the steady state

compliance J_e of coating compositions comprising 48.5 wt% of the oligomer mixtures resulting from the synthesis in Table 3, 48.5 wt% of ethoxylated Nonylphenol acrylate (ENPA) and 3 wt% of Irgacure 184. Below the method of determination of J_e is given.

5 Determination of the steady state compliance (J_e)

Instrument and measurements

The steady state compliance (J_e) was determined from dynamic mechanical measurements. These dynamic mechanical experiments were performed with a Rheometric Scientific (now TA instruments) ARES-LS rheometer equipped with a dual range 200-2000 g*cm force rebalance torque transducer, a 25 mm Invar parallel plate geometry, a nitrogen gas oven and a liquid nitrogen cooling facility. At the start of the experiments, the resin sample was loaded between the parallel plate geometry of the rheometer at room temperature. The plate-plate distance was set to 1.6 mm. After closing of the gas oven, the sample was purged with nitrogen gas for about 5 minutes.

The experiment was run by performing isothermal frequency sweeps with angular frequencies between 100 and 0.1 rad/s (3 frequencies per decade, measured in decreasing order) at 5°C temperature intervals, starting with 20 °C and lowering the temperature in 5 °C steps until the sample becomes too stiff for the instrument to measure (for the cited examples this limit is typically passed between about -20 °C and about -30 °C). Care had to be taken that the applied strains are well within the linear viscoelastic range. A typical value for the strain amplitude at room temperature is about 20-40 %, decreasing to values as low as 0.01-0.02 % at the lowest temperatures. The dynamic modulus ($G^* = (G'^2 + G''^2)^{0.5}$) and the phase angle (δ) were collected as a function of the angular frequency. Data points for which the tangent of the phase angle ($\tan\delta$) is negative (due to noise) are removed from the set.

Construction of a master- curve via time-temperature superposition

The results of the frequency sweeps (the dynamic modulus G^* and the phase angle δ as functions of the angular frequency ω), collected at various temperatures T , were combined into a so-called master curve via time-temperature superposition, following the work by Ferry (J.D. Ferry, 'Viscoelastic properties of polymers' (1980), John Wiley & Sons Inc.). As reference temperature (T_{ref}) 20 °C was chosen. For this purpose the commercial rheology data analysis software package

IRIS™, developed by Winter et al. was used.

Dynamic properties measured at lower temperatures (T) were shifted to higher frequencies to connect to the data collected at the reference temperature (T_{ref}). The horizontal shift factor a_T was determined by shifting the curves of the phase angle and of the dynamic modulus along the logarithmic angular frequency axis, following equations 1 and 2:

$$\delta(\omega, T) = \delta(a_T \omega, T_{ref}) \quad (1)$$

$$G^*(\omega, T) = G^*(a_T \omega, T_{ref}) \quad (2)$$

10

Care was taken that a good superposition of the curves of both the phase angle (δ) and the dynamic modulus (G*) was simultaneously obtained. Generally this is possible for the materials according to this invention. An often used, but optional, vertical shift factor b_T along the viscosity axis was not allowed in this work.

15

Extraction of the steady state compliance.

For the extraction of the steady state compliance the dynamic master curve was re-plotted in a different format. The storage compliance J' (=G'/G*²) and the loss compliance J'' (=G''/G*²) were plotted as a function of the angular frequency. Both the rheology data analysis package IRIS™ (commercially available from IRIS Development, 14 Elm Street, Amherst, MA 01002-2007, USA) and the Rheometric Scientific rheometer control software Orchestrator™ can be used for this conversion of the data. The mathematical details can be obtained from Ferry (J.D. Ferry, 'Viscoelastic properties of polymers' (1980) John Wiley & Sons Inc.).

25

The curve of the storage compliance typically shows a plateau at low angular frequencies, but may be prone to noise. Therefore, care has to be taken that data at too low frequencies are not included in the analysis. Data points at frequencies lower than the frequency at which the tangent of the phase angle (tanδ) exceeds 100 are removed from the master curve since the rheometer is not capable to measure accurate values of the storage compliance is the loss compliance is two decades or more larger than the storage compliance. The plateau value of the storage compliance J' is typically found at angular frequencies of 500-2000 rad/s.

30

In order to remove noise from the data we extract the value the steady state compliance via the following procedure. The software package IRIS™ version 7 is used to calculate the relaxation time spectrum from the master curve, using

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a minimum number of modes following the parsimonious model of Winter et al., which has been implemented in the IRIS software (Winter H.H., Baumgärtel M., Soskey P. 1993 'A parsimonious model for viscoelastic Liquids and solids', in A.A. Collyer Ed. 'Techniques in Rheological Measurement', Chapman & Hall, London). For the

5 examples in this application typically less than one relaxation time per decade in frequency of the master curve is used. As output of this spectrum calculation, the values for the zero shear viscosity and the steady state compliance are obtained. The accuracy for the steady state compliance determined following this method is typically $\pm 10\%$.

10

Table 3.

Molar ratio difunct.:trifunc. or difunc.:tetrafunc. oligomer	IPDI (g)	TP30LW (g)	PP50 (g)	HEA (g)	Acclaim 4200 (g) (MW 4000)	Desmophen 2061BD (g) (MW 2000)
100:0	83.48			43.6		372.22
85:15	83.78	5.82		36.18		373.52
50:50	84.12	12.65		27.45		375.07
85:15	83.85		6.87	34.73		373.85
50:50	84.20		13.32	26.38		375.40

Table 4.

Molar ratio difunctional:trifunctional or difunctional:tetrafunctional oligomer	Calculated molecular weight (g/mol)	J_e (MPa ⁻¹) of composition 48.5 : 48.5 : 3 wt% oligomer:ENPA :Irgacure 184
100:0: pure difunctional	2660	4.0
85:15 difunctional/trifunctional	3445	7.2
50:50 difunctional/trifunctional	5278	22
85:15 difunctional/tetrafunctional	3839	10
50:50 difunctional/tetrafunctional	6592	> 100

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The data of Table 4 show that the M_w of the oligomer (or mixture of oligomers) is dependent on the number of molecular chains extending from the branch point in the polyol and the ratio difunctional/trifunctional or difunctional:tetrafunctional.

The results of Table 4 indicate that the steady state compliance J_e , which is a measure of the elasticity of the liquid composition, increases with an increasing amount of tri/tetrafunctional oligomer in the composition (J_e increases going from 100:0 via 85:15 to 50:50 difunctional:tri/tetrafunctional) and with the number of
5 molecular chains extending from the branch point (J_e is higher for mixtures with tetrafunctional oligomers) . The elasticity is an important parameter, in particular for secondary resin compositions: a higher J_e often results in an improved wet-on-wet processability.

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